Complementary Study to Determine the Thermodynamic Properties of Wüstite in Deep Earth Layers up to 140 GPa

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Abstract: In this research was studied the change of Debye temperature with pressure change of the purpôleFeO, this is based on previous values of the elastic properties of this oxide, which were available in the study by S.Tlili et al 2017. And based on the idea of linear change of this parameter between every two successive pressure values, their values are determined for specific pressure values from the PREM model. Therefore, we were able to continue studying some parameters of the thermodynamic properties with changes in temperature and at these pressures. These parameters are represented by two energies internal and free, heat capacity and entropy. We found a clear effect of the Debye temperature on the phase transformation of the oxide, its value is estimated at 712.01 K at zero pressure and its values for its B1 phase are always increasing and greater than its values for its B8 phase, which increases to only 120 GPa. Moreover, at the same pressure and at a temperature of 300 K, the values of the studied thermodynamic parameters respectively are: 5.61, -3.34 kJoule/mole, 38.32 and 35.08 kJoule/K.mole, the same as before. The values of energy and heat capacity at constant volume increase in the same direction as the change with increasing temperature, in addition to the change in pressure, which increases the values of these parameters decrease. As for entropy, it takes the same change as the three parameters until a limit close to the end of the Earth's upper mantle and the beginning of the Earth's lower mantle, to begin to reverse the direction of all of that.

Keywords: wustite, Debye temperature, PREM model, thermodynamic properties

I- Introduction:

Many works interested in the Earth sciences have shown that the Earth's internal divisions consist of a large group of pure poles, such as: Al_2O_3, CaO, MgO, BaO, FeO, etc, which may be free [1] or combined with some of them in specific proportions, forming the most important minerals, such as: Olivine, Spinelle, Péridotites, Pyroxène, and Magnésiowüstite [2]. The last of these minerals, or Magnésiowüstite, is considered the most important mineral that makes up the Earth's lower mantle [3], it is composed of a superposition of magnesium oxide (MgO) or what is known as periclas and iron oxide (FeO) or what is known as wüstite [4]. Therefore, this oxide is very important, especially in this direction, and many studies have focused on it, including the works of: Brown et Shankland 1981 [5], T. Yagi et al 1988 [6], Y. Fei et H. Mao 1994 [7], S. Stølen et F. Grønvold 1996 [8], Svein Stolen et al 1996 [9], M. Murakami et al 2004 [10], JindˇrichKolorenˇc and LubosMitas 2008 [11], [12] Haruka Ozawa et al 2010, R. A. Fischer et al 2011 [13], F. Schrettle et al 2012 [14], S.Tlili et al 2017 [15], Ryosuke Tanaka et al 2020 [16] and Zhen Zhang et al 2022 [17].

As the experimental techniques or computational methods used in these studies differed, their interest differed in terms of the properties studied. However, upon closer examination, those who are most interested in thermodynamic properties find:

The study of Brown and Shankland 1981 [5]: This work constitutes a great reference in the determination of the thermodynamic state of the earth where they propose an approach based on the Debye Model with two cut-off frequencies for compression waves and shear in order to deduce some thermodynamic parameters and draw up a profile for the earth's structure from seismological data (Parametric Earth Model). Also, they have application for a variety of solids. This work is essential as it presents the change in density and the three wave speeds by the change in pressure at the limit of our study where we will make a comparison with its results.

The study of S. Stølen and F. Grønvold 1996 [8]: In this study, the phase boundaries of high-pressure wüstite are calculated using a thermodynamic data set describing the Fe-O system. A new thermodynamic description of wüstite is presented, while the thermodynamic descriptions of iron, oxygen, magnetite and hematite are taken from the literature. The equation for the Gibbs energy for the formation of wüstite at ambient pressure is based on calorimetric studies. The description gives reasonable values for the eutectic point and phase boundaries of wüstite at high temperatures and further explains the formation of a metastable intermediate mixture of almost stoichiometric wüstite and magnetite upon heating quenched wüstite to approximately 500 K. extrapolation to high pressures is made taking into account the variation in composition, temperature and pressure of the molar volume of wüstite. Also, she presented the variation of this modulus as a function of the x value in this oxide otherwise between 88 to 100. Thus she showed the change in the volume of the structural mesh.

Svein Stolen et al 1996 [9]:This study was concerned with a three-phase sample of Feo.99o:to.oosO, Fe_30_4 and Fe (mole fractions 0.915, 0.078 and 0.007, respectively), where the heat capacity of a sample was measured by adiabatic shield calorimetry at temperatures ranging from 13 to 450 Kelvin. $FeO_{.990}$ and magnetite are formed as metastable intermediates upon heating of asymmetric quenched wisterite with composition $FeO_{.93740}$. The small amount of Fe originates from the second disproportionation reaction, in which a stable two-phase mixture of Fe and magnetite is formed from $FeO_{.990}$. The value of ~Sm ($FeO_{.990}$ 298.15 K), 60.45 J/(K. mol), is derived from the three-phase sample entropy and the recommended standard entropy for iron and magnetite. The nature of the magnetic order disorder transition changes with composition and is strongly cooperative in $FeO_{.990}$ with TN ~ 191 K. A slight higher order transition is observed at 124 K. This occurs due to the Verwey transition in magnetite, this magnetite, formed in equilibrium Metastable with $FeO_{.990}$, presumably more Fe-rich than magnetite in stable equilibrium with Fe.

Zhen Zhang et al 2022 [17]:This study confirmed the importance of FeO in the Earth's core, as it proved that its thermodynamic properties are essential for developing more accurate core models. It also showed that it is also a notoriously cross-linked insulator in the NaCl phase of type (B1) at ambient conditions. It undergoes two polymorphic transitions at 300 K before becoming metallic in a NiAs-type (B8) structure at 100 GPa. Although its phase diagram has not been fully mapped, it is well established that the B8 phase transforms into a NiAs-type (B8) phase, B2 or CsCl-type at basic pressures and temperatures. You get a successful calculation from the beginning of the B8 to B2 phase boundaries in FeO at Earth's fundamental pressures. It is also shown that completely inharmonic free energies calculated using the PBE-GGA + Mermin function reproduce the experimental phase boundaries within uncertainties at $P > 240$ GPa, including a largely negative Clapeyron slope of -52 ± 5 MPa/K. Finally, their study achieves the possibility of applying the standard DFT function to FeO under Earth's fundamental conditions and demonstrates a theoretical framework that enables complex predictive studies of this region.

It is noted that these studies did not cover all the thermodynamic parameters and how they develop depending on the change in temperature and pressure in the subsurface. These are two variables that are precisely determined according to seismology. This science is considered one of the most important earth sciences that is concerned with the mineral composition of the Earth's interior [18]. This is after dividing the Earth into layers through the PREM model [19], and the temperatures for each depth were determined through studies, the most important of which is [20].

The study by Tlili et al 2017 [15] can be considered one of the studies interested in studying this oxide, and it is one of the studies that dealt with it from the point of view of seismology. In this work, they carried out calculations using the density functional pseudopotential method to obtain precise information about FeO, exactly about its structural and elastic properties, as well as a comparison with its values obtained from some studies and the PREM model in the pressure range 0-140 GPa at 0 K. The important points to remember from the above are; By changing the pressure, we notice that at 77 GPa, this oxide passes from the cubic NaCl phase (B1) to the hexagonal NiAs phase (B8) with an increase in density of approximately 5%. Only the study of the density, mass modulus and speed of the overall sound wave shows continuous curves, which means that there is no occurrence of the phase transition. They found a linear dependence in increasing density, most elastic constants, and modulus or wave velocities of FeO with increasing pressure. But C44 in phase B1, c66, shear modulus and transverse wave speed in phase B8 are not correlated with the previous trend. These special results for elastic constants reveal that the changes of c11 and c12 in the first phase and each of c33 and c13 in the second phase are within the limits established by previous studies of pure poles contained in the lower mantle.

In these papers, we will correct the shortcomings resulting from previous studies on iron oxide, which are represented in determining the Debye temperature values. Thus, we determine the values of some parameters of the thermodynamic properties,these parameters are represented by the internal and free energies and the heat capacity when the volume constant and entropy. Thus, we determine the values of some parameters of the thermodynamic properties, these parameters are represented by the internal and free energies and the heat capacity when the volume constant and entropy. Based on the study by S.Tlili et al 2017 [12], which provides the necessary property values needed to calculate the Debye temperature, Either at the pressures adopted in that study or at the pressures of the PREM model. Therefore, the thermodynamic coefficients are calculated in addition to their change in temperature, it will take place at specific pressures. All of this is by presenting the method of calculating these characteristics in such studies, Followed by interpretation and discussion of the results, and finally a conclusion summarizing all of this.

II- Method of calculating thermodynamic properties:

The calculation method for determining the dynamic properties depends on the following four steps:

1- Calculating the values of the structural properties of the material and thus determining the density of the material or its volumetric mass, which in our study is given by the following relationship:

$$\rho = Z\frac{M_{O^{-2}} + M_{Fe^{+2}}}{N_A V_C} \qquad (1)$$

Where: VC is the volume of the conventional cell, taken in cubic centimetres, M_(Fe^(+2)) and M_(O^(-2)) is the molar mass of the iron ion and oxygen ion, respectively, taken in grams, Z is the number of nodes in the conventional cell. .

2- Calculating the elastic properties, especially their constants Cij, of the material. Therefore, the volumetric compression coefficients B and shear G can be calculated according to the Voigt & Russ method [20, 21] and the average is calculated using the Hill method [23].

These two steps are based on the density functional theory (DFT). This theory is the most widely used method in quantum mathematical operations to solve the Schrödinger equation because of its possibility of applying to various systems (multivariable) [24]. The program CASTEP is based on this theory [25], which uses several approximations including; The local density approximation (LDA)[26] and the generalized gradient approximation (GGA)[27]. If this approximation improves the accuracy of the first approximation, moreover, one of the functions available within these two approximations can be adopted.

3- The calculation can be easily completed to determine the values of the velocities of the longitudinal waves VP and the transverse waves VS using the following two relationships [15]:

$$V_P = \sqrt{\frac{3B + 4G}{3\rho}} \qquad (2)$$

and

$$\mathbf{V_S} = \sqrt{\frac{\mathbf{G}}{\boldsymbol{\rho}}} \tag{3}$$

4- Now, by being satisfied with the value of the density and speeds of the two waves specified above, the value of the Debye temperature can be calculated, as it is given by the following relationship [28]:

$$\boldsymbol{\theta}_{\mathbf{D}} = \frac{\mathbf{h}}{\mathbf{k_B}}\left[\frac{\mathbf{9nN_A}\boldsymbol{\rho}}{\mathbf{4}\boldsymbol{\pi}(\mathbf{M_{O^{-2}}} + \mathbf{M_{Fe^{+2}}})\left(\frac{\mathbf{1}}{\mathbf{V_P}^{2}} + \frac{\mathbf{2}}{\mathbf{V_S}^{2}}\right)}\right]^{\frac{1}{3}} \tag{4}$$

Where h is Planck's constant and kB is Boltzmann's constant, while n is the number of atoms in the primary cell of the crystal, which is estimated here at 2.

5- It has also become possible to calculate the values of thermodynamic properties based on their change in temperature, the most important of which are:

A- Internal energy: It is calculated from the following relationship [29]:

$$\boldsymbol{E} = \mathbf{9}\boldsymbol{RT}\left(\frac{\mathbf{1}}{\boldsymbol{x_D}}\right)^{3}\int_{0}^{x_D}\frac{\boldsymbol{x}^{3}}{\boldsymbol{e}^{x} - \mathbf{1}}\boldsymbol{dx} \tag{5}$$

and

$$\mathbf{x_D} = \frac{\hbar\boldsymbol{\omega_D}}{\boldsymbol{k_B T}} = \frac{\boldsymbol{\theta_D}}{\boldsymbol{T}} \tag{6}$$

R is the gas constant, T is the temperature, *ℏ* is the Planck constant, and ωD is the vibration frequency.

B- Free energy: It is calculated according to the relationship [29]:

$$\boldsymbol{F} = \mathbf{9}\boldsymbol{RZT}\int \boldsymbol{x}^{2}\,\mathbf{ln}\left(\mathbf{1} - \boldsymbol{e}^{-\frac{\theta_D}{T}x}\right)\boldsymbol{dx} \tag{7}$$

C- Heat capacity with constant volume: It is calculated according to Debye's law. The mathematical formula for heat capacity can be written in the following form [29]:

$$\boldsymbol{C_V} = \frac{\boldsymbol{dE}}{\boldsymbol{dT}} = \mathbf{9}\boldsymbol{R}\left(\frac{\boldsymbol{T}}{\boldsymbol{\theta_D}}\right)^{3}\int_{0}^{\theta_D/T}\frac{\boldsymbol{x}^{4}\boldsymbol{e}^{x}}{(\boldsymbol{e}^{x} - \mathbf{1})^{2}}\boldsymbol{dx} \tag{8}$$

D- Entropy: It is calculated based on the second principle of thermodynamics according to the following relationship [30]:

$$\boldsymbol{S} = \int\frac{\boldsymbol{\delta Q}}{\boldsymbol{T}} = \int \boldsymbol{c_v}\frac{\boldsymbol{dT}}{\boldsymbol{T}} = \mathbf{9}\boldsymbol{RZ}\frac{\boldsymbol{\theta_D}}{\boldsymbol{T}}\int \boldsymbol{x}^{3}\left[\frac{\mathbf{1}}{\boldsymbol{e}^{\frac{\theta_D}{T}x} - \mathbf{1}} - \mathbf{ln}\left(\mathbf{1} - \boldsymbol{e}^{-\frac{\theta_D}{T}x}\right)\right]\boldsymbol{dx} \tag{9}$$

In order to change the pressure allowed by the CASTEP program used, all previous steps must be completed after determining the material stability pressure ranges. That is, the possible stable phases must be known in the field of study as a whole, by knowing the enthalpy change of formation or heat content H equal to the free energy ΔG of crystal formation at absolute zero at which the calculation is done in our case. Where [15]:

$$\boldsymbol{\Delta G} = \boldsymbol{H} + \boldsymbol{TS} = \boldsymbol{H} + (\mathbf{0})\boldsymbol{S} = \boldsymbol{H} \tag{10}$$

6- As for accurately determining the values of the parameters studied at certain pressures, such as the pressure values of the PREM model, there are multiple methods, including those that enable any function in a certain field to be compensated or approximated to another function. Among these frequently used polynomial functions, the type often known as generation or polarization can be used here. However, it is possible to prefer the linear change occurring between every two successive points, as we search each time for the magnitudes of both the slope of the change a and its initial value b, that is, we use the following equation:

$$\boldsymbol{P(x) = ax + b} \tag{11}$$

7- Finally, to calculate integrals, there are various numerical methods that depend on repeating certain operations, including the trapezoidal method, which was developed into the Romberg method. The latter is characterized by a lower number of repetitions and high accuracy [31].

III- Results and interpretation:

III-1 Debye temperature:

In fig. 2 the change of the Debye temperature for FeO is presented by changing the pressure values used in the work of [15] tlili et al. 2017 and its values in the PREM model, while in Table. 1 its values are presented at the boundary pressures of the most important parts of the Earth's interior. From which it becomes clear that:

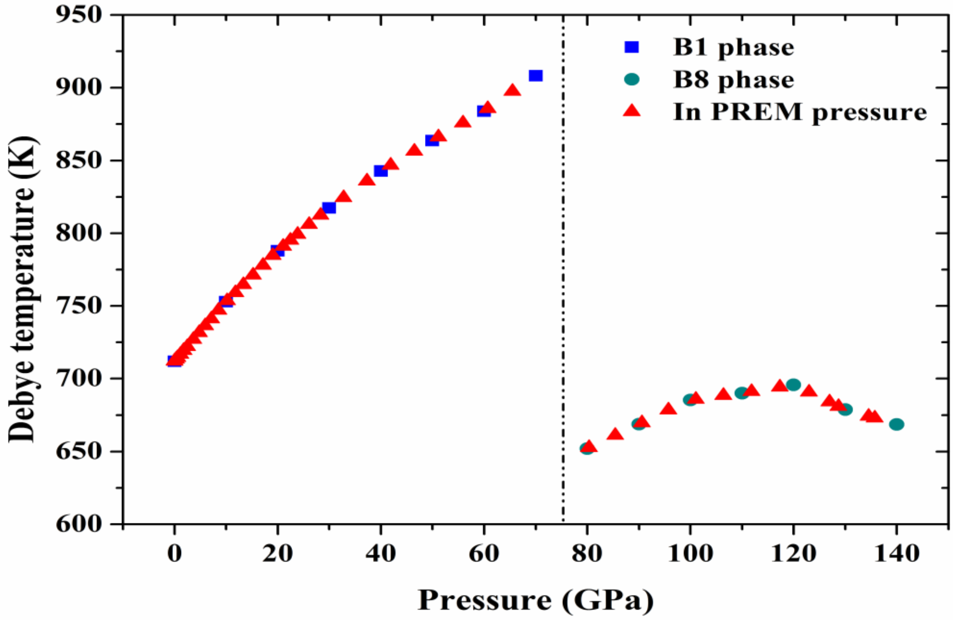

Figure 1: Debye temperature change for FeO with pressure changes used in the work of S.Tlili et al 2017 [15] and that available in the PREM model

The Debye temperature values of this oxide are greatly affected by its phase change, so they have different values in many respects.

Within the limits of the first phase of the oxide, the Debye temperature values increase non-linearly, but the linear change appears in two regions, the first of which is in the Earth's crust and upper mantle, and the other is from the beginning of the Earth's lower mantle until the end pressure of this phase's stability.

In the second phase, the change in Debye temperature values takes the form of an almost parabolic piece, as it increases starting from the pressure at which this phase begins to stabilize until the pressure is 120 GPa. At this pressure, its value reaches the maximum value in this phase, and from there it begins to decrease until the last pressure in this study. With a more precise observation, there is an almost linear change in three regions (1.67 K/GPa); The first is between the pressures of 80 and 100 GPa, with a slope that is smaller by more than a third of the previous one (0.52 K/GPa), and finally between the pressures of 120 and 140 GPa, with a decreasing slope (1.36 K/GPa).

In addition, the Debye temperature values in the first phase of the oxide are always higher than their values in the second phase, as its highest value, estimated at 695.73 K, which appears at the aforementioned pressure of 120 GPa, is 16.28 K lower than its lowest value in the first phase, which is At 120 GPa.

After determining the Debye temperature with a change in pressure in the PREM model, we found that it is: It increases in both the Earth's crust and the Earth's upper mantle, respectively, by about 10 and 77 K. While it decreases in the Earth's lower mantle by 127 K, but inevitably after passing through it, an increase of up to 127 K at a pressure of 65.5202 GPa and a decrease of about 245 K at a pressure of 80.366 GPa. GPa, finally increasing to 20 K at pressure 135.7509 GPa (see Table. 1).

Also, this last determination of the Debye temperature at pressure values enables us to determine the values of the thermal properties with great accuracy, and it also helps us in simplifying the remaining study.

Table 1: Values of the internal and free energies parameters, heat capacity and entropy at the depth, pressures and temperature of the basic boundaries studied from the Earth's interior to the Gothenburg region for FeO.

Depth (km)	Pressure (GPa)	Debye temperature (K)	Temperature (K)	Internalenergy (kJoule/mole)	Heat capacities (Joule/K.mole)	Entropy (Joule/K.mole)	Free energy (kJoule/mole)
0	0	712,01	300	5,62	38,32	35,08	-3,34
			1000	51,28	49,21	62,21	-71,04
80	2,4539	722,04	300	5,62	38,32	35,08	-3,34
			1000	51,12	49,19	62,16	-70,32
80	2,4546	722,04	1000	51,12	49,19	62,16	-70,32
			1600	80,78	49,61	62,68	-133,64
670	23,8334	799,22	1000	49,90	49,01	61,69	-65,19
			1600	79,49	49,53	62,71	-125,50
670	23,8342	799,22	1600	79,49	49,53	62,71	-125,50
			2488	136,89	49,81	61,88	-266, 77
/	65,5202	897,31	1600	77,87	49,41	62,65	-116,39
			2488	135,19	49,76	62,22	-251,02

/	80,366	652,07	2620	159,97	49,89	60,65	-355,06
			4700	236,54	49,94	59,04	-599,77
2891	135,7509	672,89	2620	159,61	49,88	60,77	-350,16
			4700	236,17	49,93	59,17	-592,52

In this table, the values are equal at the borders of the separation between the ground layers within the scope of our study. This equality is approximate because the difference is very small, as stated in the text.

III-2 Internal energy:

From figs. 2-5(part A), for all pressures, the internal energy values increase linearly with increasing temperature, with very similar tendencies, as they are limited to 49.92 joule/K.mole for the pressure of 80.366 GPa and 46.84 joule/K. mole at pressure 2.4539 GPa.

At the first pressure mentioned above, which is in the lower Earth's mantle, the values of this energy are the highest, while for the second pressure, which is in the Earth's crust, the values of this energy are the lowest (confirm in table. 1).

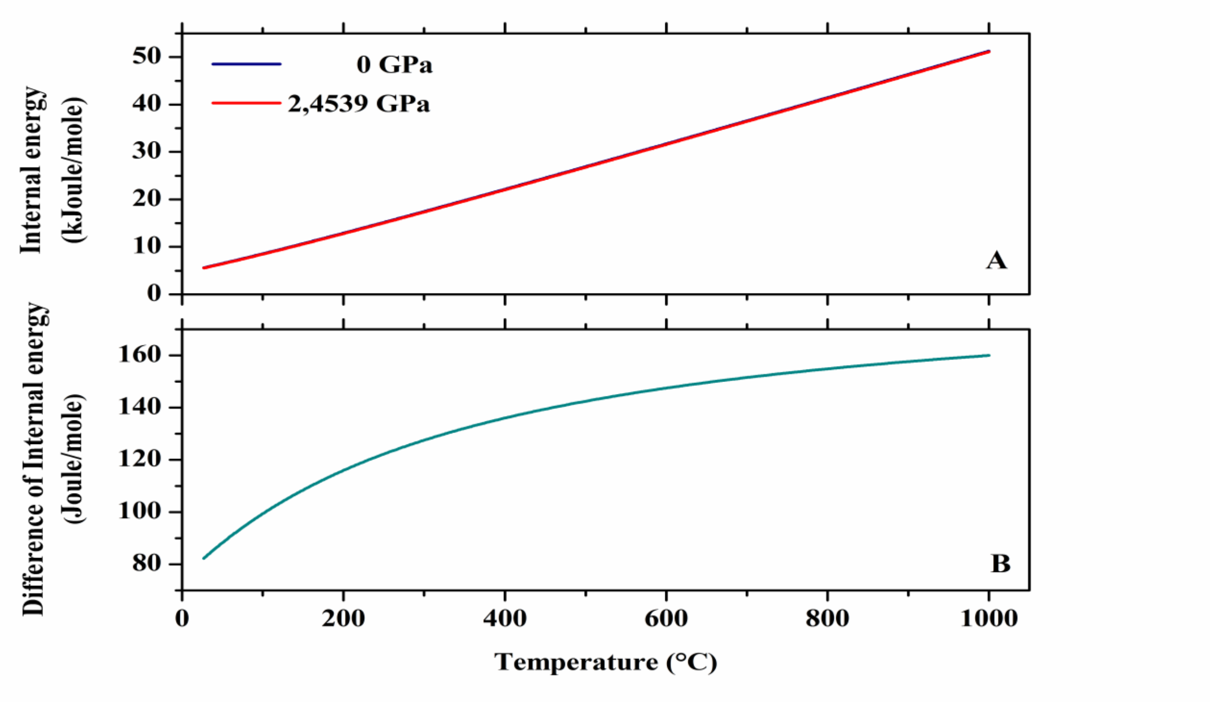

Figure 2: A- Change in the internal energy values of FeO with changes in both temperature and pressure at the boundaries of the Earth's crust

B- Change in the values of the difference in the internal energy of FeO between the two pressures of the Earth's crust boundaries with change in temperature

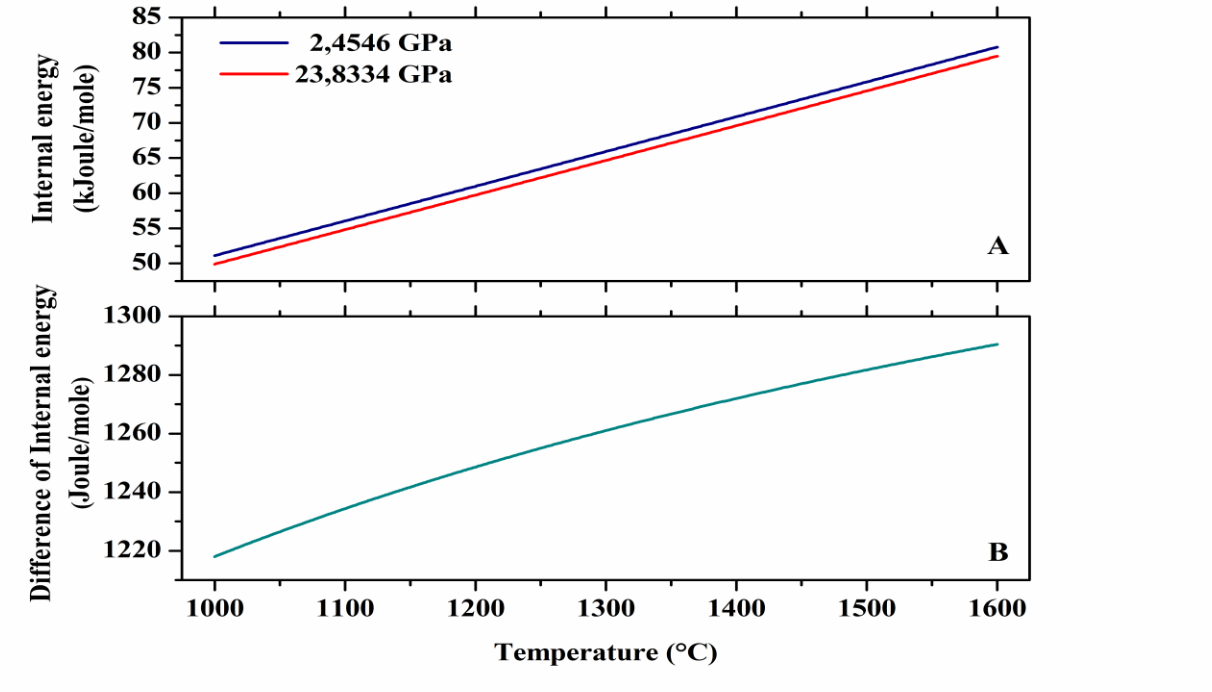

Figure 3: A- Change in the internal energy values of FeO with changes in both temperature and pressure at the boundaries of the Earth's upper mantle

B- Change in the values of the difference in the internal energy of FeO between the two boundary pressures of the Earth's upper mantle with change in temperature

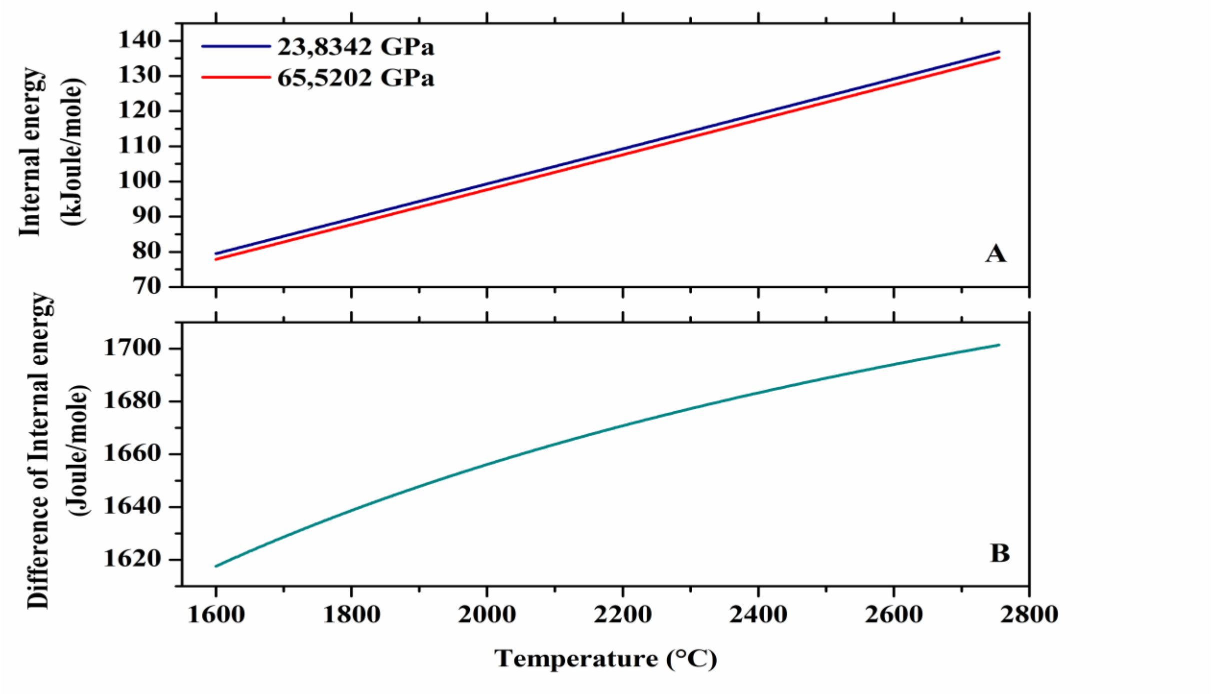

Figure 4: A- The change in the internal energy values of FeO with changes in both temperature and pressure at the beginning of the Earth's lower mantle until the end of the stability of the B1 phase of the oxide

B- Change in the values of the difference in the internal energy of FeO between two boundary pressures starting from the Earth's lower mantle until the end of the stability of the B1 phase of the oxide with a change in temperature

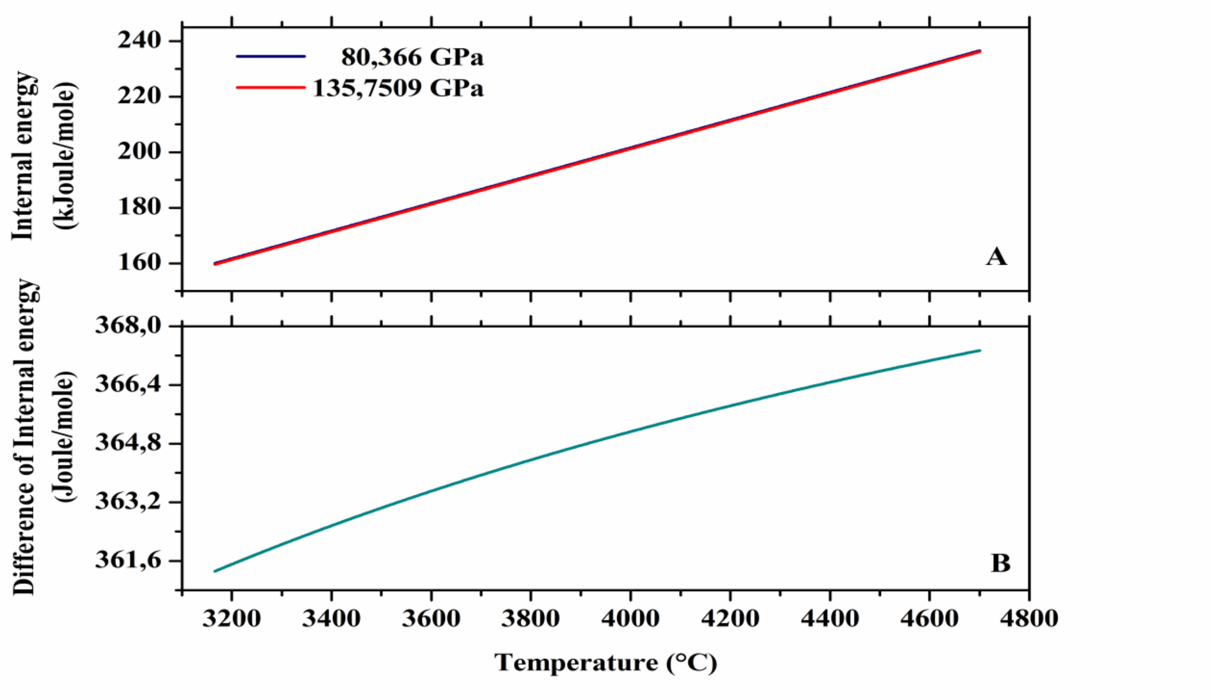

Figure 5: A - Change in the internal energy values of FeO with changes in both temperature and pressure at the limits from the beginning of the stability of the B8 phase of the oxide until the end of the Earth's lower mantle

B- Change in the values of the difference in the internal energy of FeO between two boundary pressures from the beginning of the stability of the B8 phase of the oxide until the end of the Earth's lower mantle with a change in temperature

Moreover, it can be noted that the internal energy of the oxide is limited to spheres, the longest of which is 80.366 GPa for pressure; Which is estimated at 76.57 kjoule/mole, and the narrowest is for a pressure of 23.8334 GPa; Which is estimated at 29.59 kjoule/mole. The values of this energy change inversely with changes in pressure, as for lower values of pressure its values are higher in the same layer. But the real limitation of the values of this energy is in the ranges, the longest of which appears for the second phase of the studied oxide and is estimated at 76.1 kjoule/mole, while the narrowest is estimated at 28.37 kjoule/mole, which occurs in the lower Earth's mantle

From figs. 2-5(part B), it appears that the difference between the energy values increases with increasing temperature, and this occurs in all ranges. The smallest difference is estimated at 82.29 joule/mole, which occurs in the Earth's crust and for a temperature of 300 K. The highest difference is estimated at 1.7 kjoule/mole, which appears in the Earth's lower mantle and at the end of the first phase of oxide and for a temperature of 300 K. The temperature is 2755 K.

This difference in each region increases almost linearly for the highest temperatures within each range, with the absence of a linear increase for the lowest temperatures, especially in the Earth's crust. The difference value also increases as the pressure value increases, that is, as the depth increases.

On the border of the Mohoroviči (Moho) regions separating the crust and the mantle and the border separating the upper and lower mantle lays the observation that the values of this energy are almost equal, as this difference between the borders of the two regions is estimated at 0.05 and 0.04 joule/mole, respectively.

III-3 Free Energy:

From figs. 6-9(part A and B) of their parts and the values recorded in table 1, it can be seen that the change in free energy with change in temperature at all pressures for this oxide corresponds to the change in internal energy, but with values that decrease in a more linear manner and with an ever-increasing difference. Where the highest and lowest values of the width of the change fields appear for the same two pressures, 80.366 GPa and 23.8334 GPa, as their values are respectively; 244.71 and 60.31 kjoule/mole. As for displaying the real fields of change, the highest of them appears in the stability field of the second phase of oxide from the Earth's lower mantle with the value 60.31 kjoule/mole, while the lowest value appears in the Earth's upper mantle with the value 237.46 kjoule/mole. The values of this energy change in accordance with the change in pressure, as from Yes, the minimum pressure values are lower in the same layer. Its highest value is at a pressure of 80.366 GPa and at 4700 K, estimated at -599.77 kjoule/mole, while its lowest value is at a pressure of 2.4539 GPa and at 300 K, estimated at -3.26 kjoule/mole. At the first pressure mentioned above, which is in the Earth's lower mantle, the tendency for this energy to decrease, which is estimated at 159.52 joule/K.mole, is the highest, while for the second pressure, which is in the Earth's crust, the value of the tendency to decrease, which is estimated at 68.92 joules. /K.mole is the lowest.

With the increase in pressure, the value of the difference between the values of this energy increases for two successive pressures, that is, the deeper we go into the Earth's interior. The smallest difference is estimated at 78.07 joule/mole, which occurs in the Earth's crust and for a temperature of 300 K. The highest difference is estimated at 15.75 kjoule/mole, which appears in the Earth's lower mantle and at the end of the first phase of oxide and for a temperature of 300 K. Temperature 2755 K.

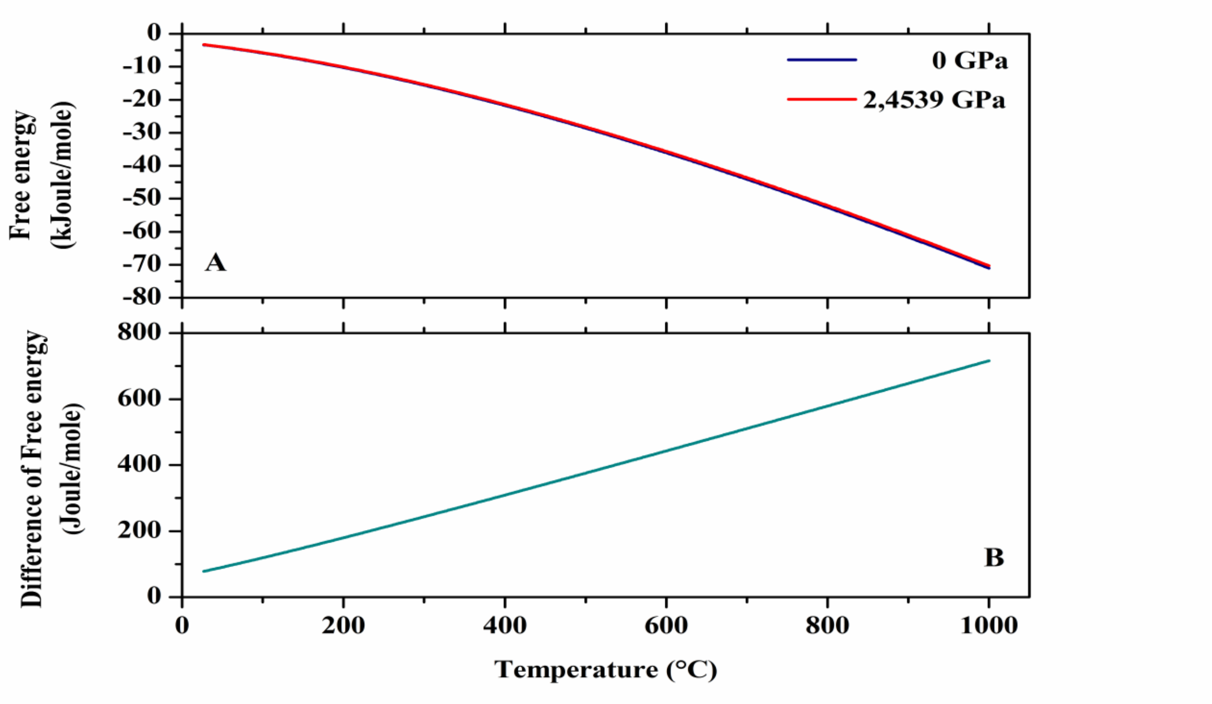

Figure 6: A- Change in the free energy values of FeO with changes in both temperature and pressure at the boundaries of the Earth's crust

B- Change in the values of the difference in the free energy of FeO between the two pressures of the Earth's crust boundaries with change in temperature

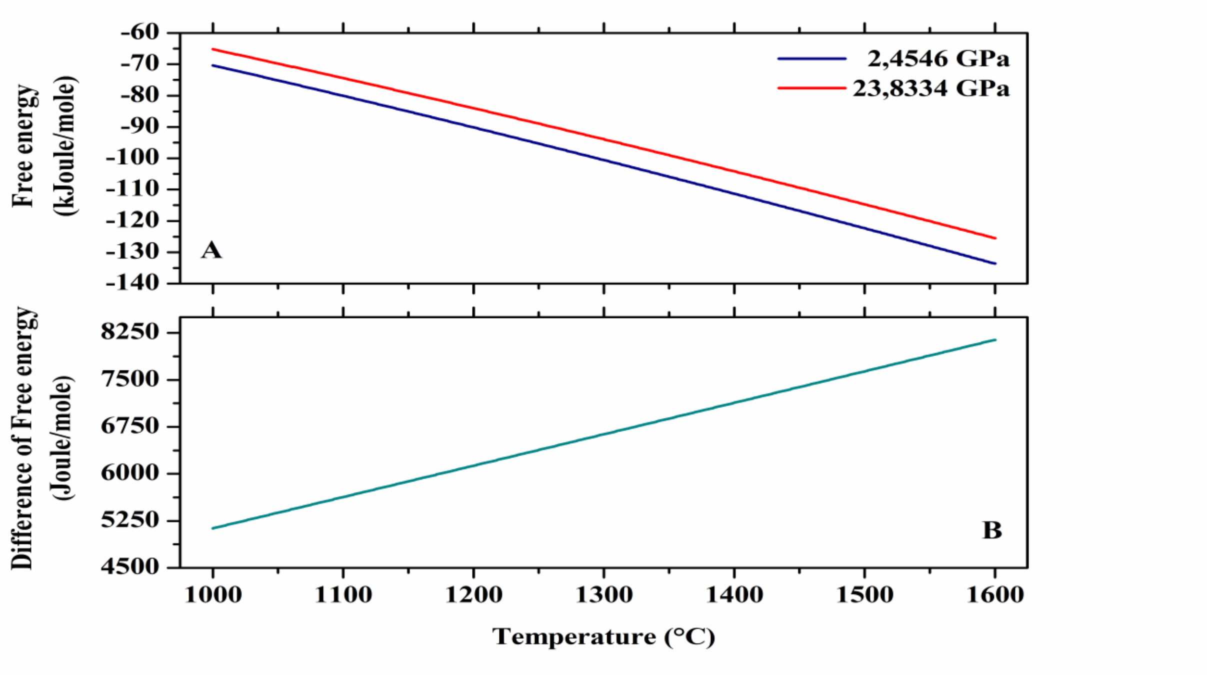

Figure 7: A- Change in the free energy values of FeO with changes in both temperature and pressure at the boundaries of the Earth's upper mantle
B- Change in the values of the difference in the free energy of FeO between the two boundary pressures of the Earth's upper mantle with change in temperature

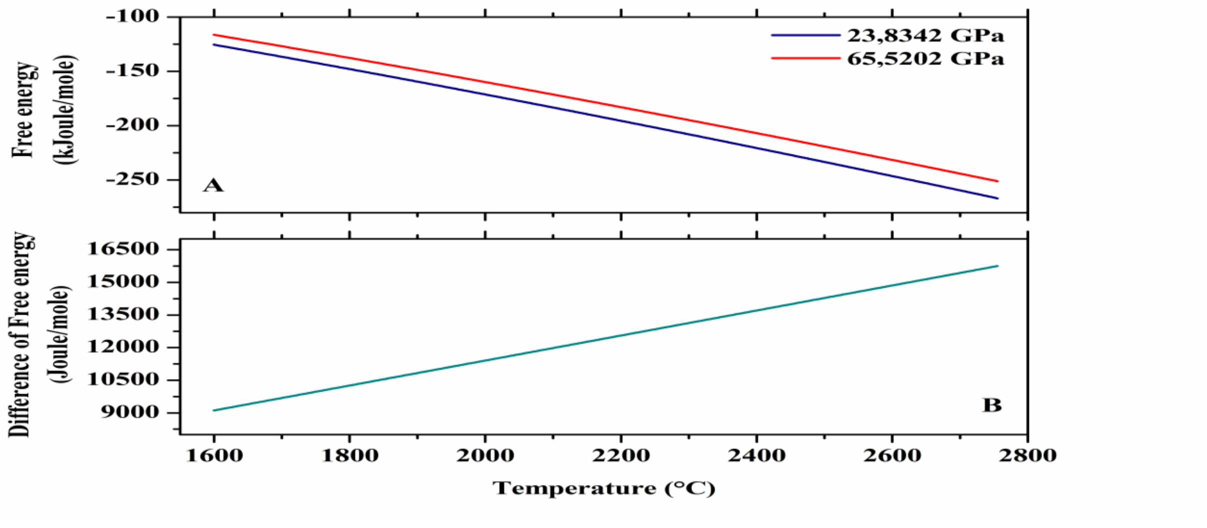

Figure 8: A- The change in the free energy values of FeO with changes in both temperature and pressure at the beginning of the Earth's lower mantle until the end of the stability of the B1 phase of the oxide
B- Change in the values of the difference in the free energy of FeO between two boundary pressures starting from the Earth's lower mantle until the end of the stability of the B1 phase of the oxide with a change in temperature

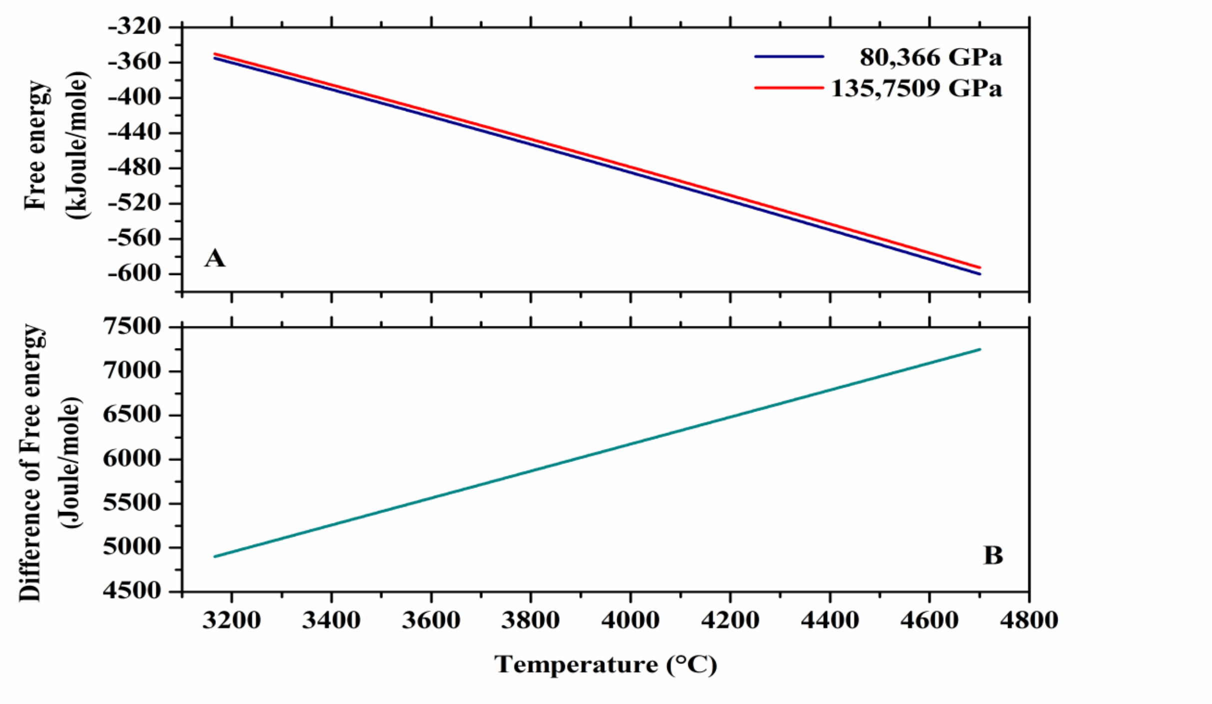

Figure 9: A- The change in the free energy values of FeO with changes in both temperature and pressure within the limits from the beginning of the stability of the B8 phase of the oxide until the end of the Earth's lower mantle

B- Change in the values of the difference in the free energy of FeO between two boundary pressures from the beginning of the stability of the B8 phase of the oxide until the end of the Earth's lower mantle with a change in temperature

At the same separating boundaries mentioned previously, the energy values are also almost equal, as this difference between the boundaries of the two regions is estimated at 0.020 and 0.023 joule/mole, respectively.

III-4 Heat capacity at constant volume:

In figs. 10-13 (part A and B) represent the change in the heat capacity at constant volumeof FeO with changes in both temperature and pressure within the limits in deep earth layers up to 140 GPa, and the values recorded in table 1.

From these figuers shapes it can be observed:

This capacity changes with changing temperature for two successive pressure values with an always decreasing difference, in a non-linear manner, especially in the Earth's crust. At this layer and for a temperature of 300 K, the difference is at its highest value, which is estimated at 0.27 joule/K.mole, while the smallest difference, estimated at 0.0027 joule/K.mole, appears in the Earth's lower mantle in the second phase of oxide at a temperature of 4700. K. The value of this heat capacity permanently increases with increasing temperature, but its values are lower the higher the pressure value. Therefore, the lowest and highest values of heat capacity at the same temperature and pressure are always 2.4539 and 80.366 GPa, respectively, which are estimated at 38.05 and 49.94 joule/K.mole, respectively as well. The values of this capacity are limited to areas of width of 10.88 and 0.47 joule/K.mole as the highest and lowest width, respectively, which also appear in the same two areas, respectively. But the lowest and highest widths of the real fields appear in the same two regions, whose values are 10.86 and joule/K.mole 0.44, respectively.

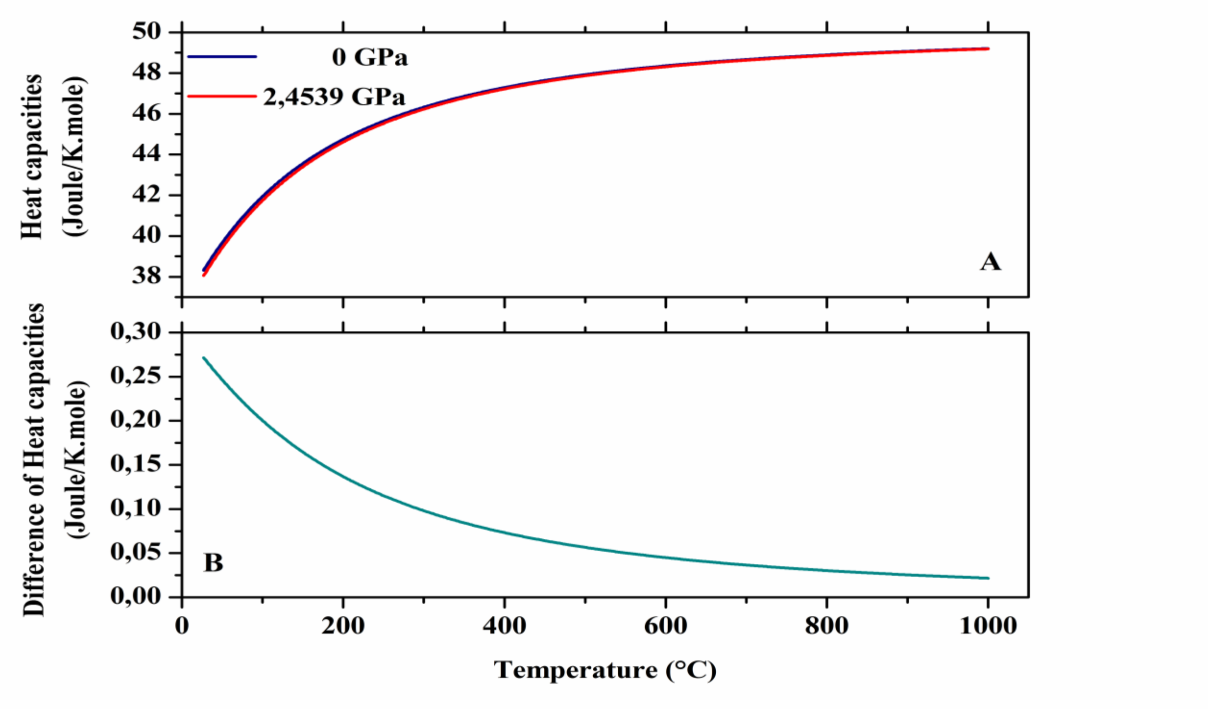

Figure 10: A- Change of heat capacity values with constant volume for FeO by changing both temperature and pressure at the boundaries of the Earth's crust

B- Change in the values of the difference in heat capacity with constant volume of FeO between the two pressures of the Earth's crust boundaries with change in temperature

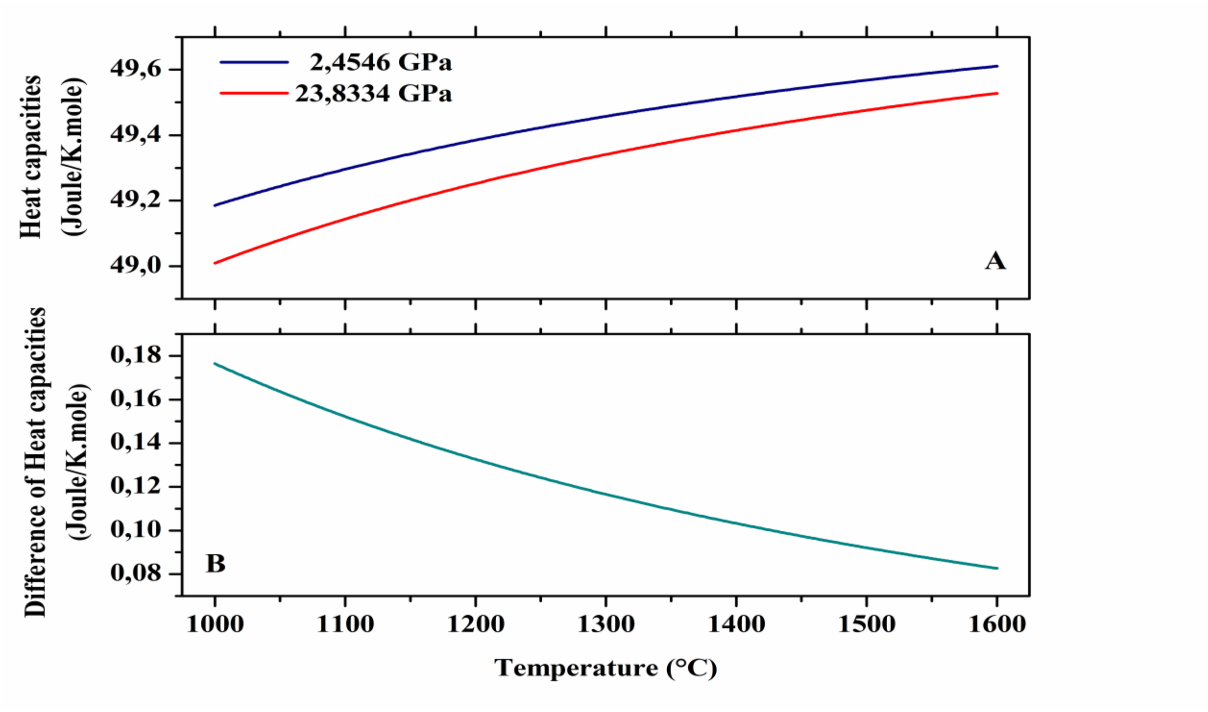

Figure 11: A- Change of heat capacity values with constant volume for FeO by changing both temperature and pressure at the boundaries of the Earth's upper mantle

B- Change in the values of the difference in heat capacity with constant volume of FeO between the two boundary pressures of the Earth's upper mantle with change in temperature

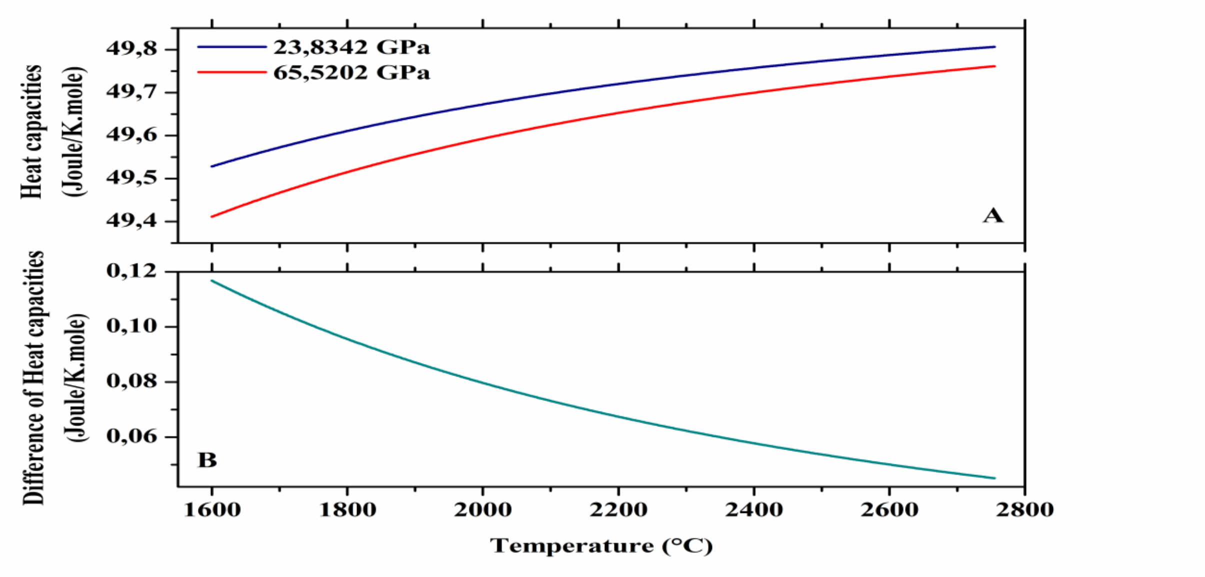

Figure 12: A - Change in heat capacity values with constant volume for FeO with changes in both temperature and pressure at the beginning of the Earth's lower mantle until the end of the stability of the B1 phase of the oxide

B- Change in the values of the difference in heat capacity with constant volume for FeO between two boundary pressures starting from the Earth's lower mantle until the end of the stability of the B1 phase of the oxide with changing temperature

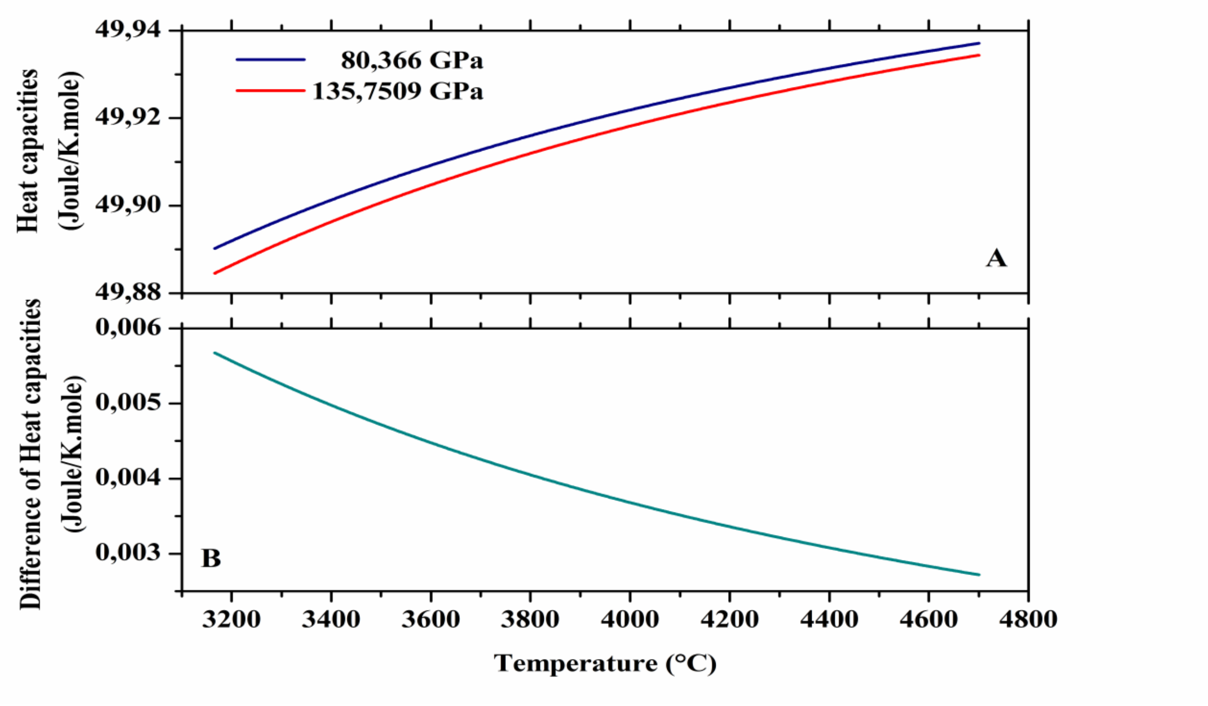

Figure 13: A- The change in heat capacity values with constant volume for FeO with changes in both temperature and pressure at the limits from the beginning of the stability of the B8 phase of the oxide until the end of the Earth's lower mantle

B- Change in the values of the difference in heat capacity with constant volume for FeO between two boundary pressures from the beginning of the stability of the B8 phase of the oxide until the end of the Earth's lower mantle with a change in temperature

The difference in energy values between the borders of the two separating regions mentioned previously is very small, meaning that their values are almost equal, as this difference is estimated at 0.021 and 0.083 joule/mole, respectively.

III-5 Entropy:

In figs. 14-17 (part A and B) represent the change in the entropy of FeO with changes in both temperature and pressure within the limits in deep earth layers up to 140 GPa, and the values recorded in table 1.

What is observed from these figures is that the longest range in which the entropy value changes is in the region of the Earth's crust, which is by the amount 27.55 joule/K.mole for the pressure 2.4539 GPa. Moreover, in this region there is an increase in the entropy value of the oxide, and this increase continues until the end of the Earth's upper mantle. It reaches a limit value estimated at 62.71 joule/K.mole at a temperature of 1460 K for a pressure of 2.4546 GPa, and it reaches a limit value estimated at 62.16 joule/K.mole at a temperature of 1600 K for a pressure of 23.8334 GPa. In these two regions, the values of this entropy for the lower pressure value are the highest up to a temperature estimated at 1552 K, so it can be observed that a non-linear decrease between the two changes begins to increase after this temperature. At a temperature of 1552 K, there is a convergence in the entropy values, which are estimated at 62.697 joule/K.mole.

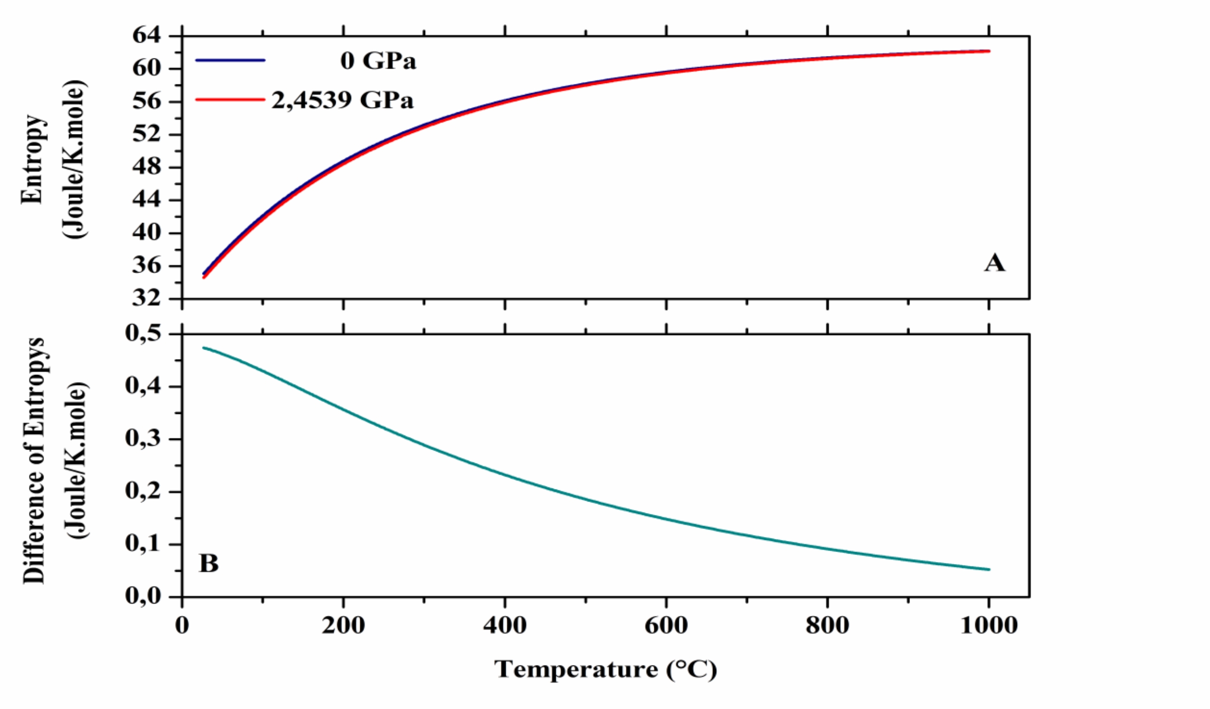

Figure 14: A- Change of entropy values for FeO with changes in both temperature and pressure at the boundaries of the Earth's crust

B- Change in the values of the entropy difference for FeO between the two pressures of the Earth's crust boundaries with changing temperature

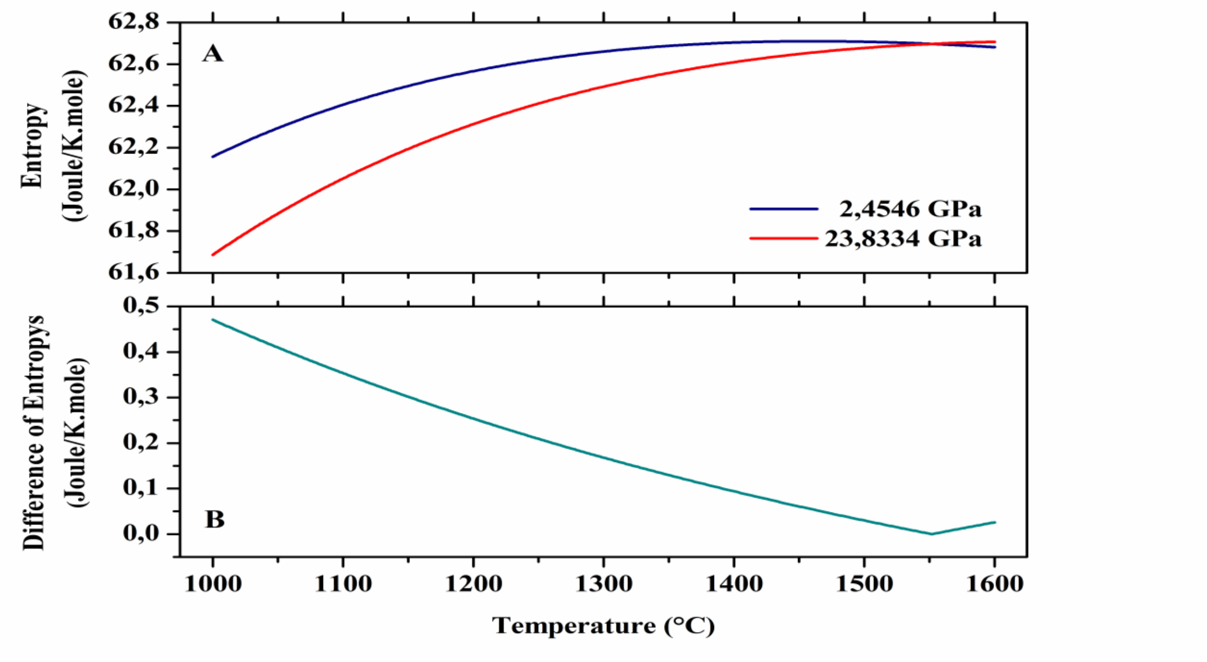

Figure 15: A- The change in entropy values for FeO with changes in both temperature and pressure at the boundaries of the Earth's upper mantle

B- Change in the values of the entropy difference for FeO between the two boundary pressures of the Earth's upper mantle with changing temperature

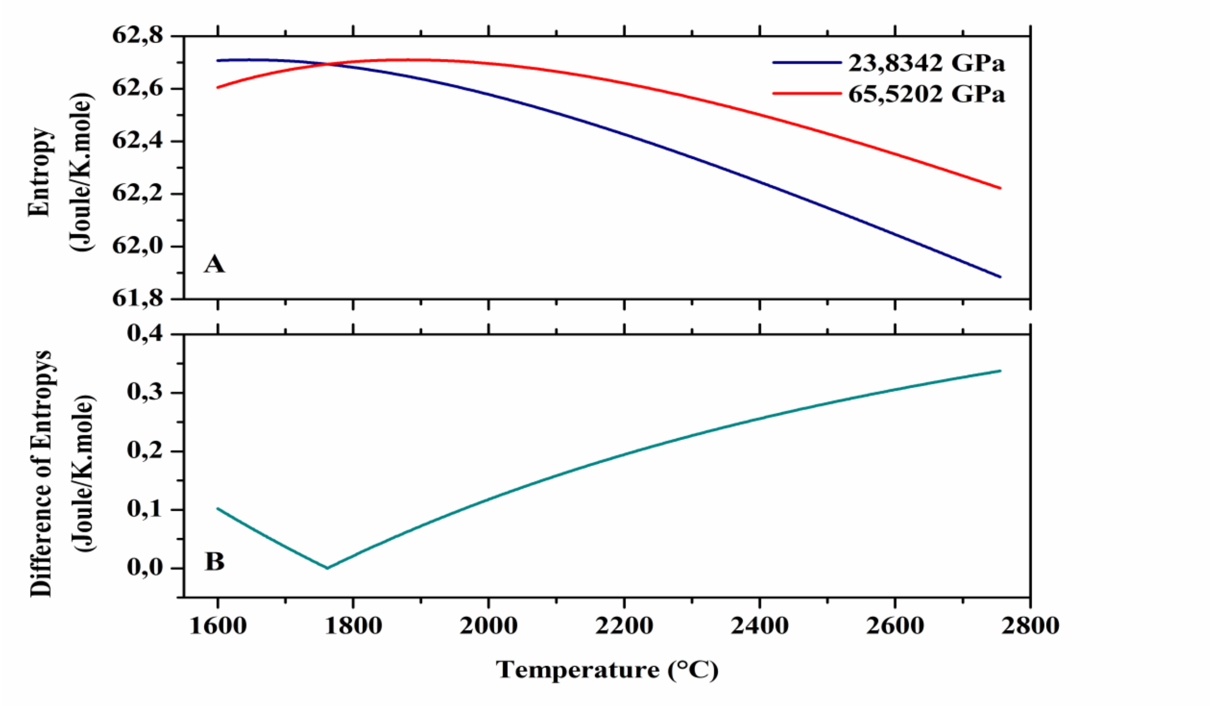

Figure 16: A- The change in entropy values for FeO with changes in both temperature and pressure at the boundaries starting from the Earth's lower mantle until the end of the stability of the B1 phase of the oxide

B- Change in the values of the entropy difference for FeO between two boundary pressures starting from the Earth's lower mantle until the end of the stability of the B1 phase of the oxide with a change in temperature

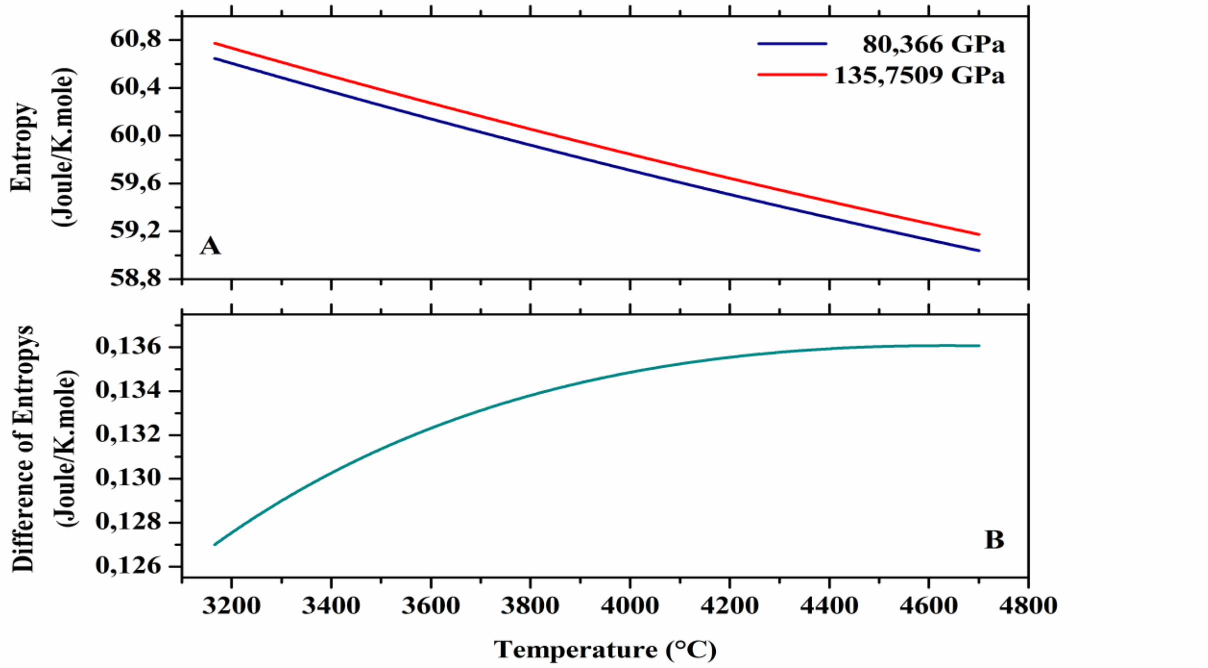

Figure 17: A- The change in entropy values for FeO with changes in both temperature and pressure at the limits from the beginning of the stability of the B8 phase of the oxide until the end of the Earth's lower mantle B- The change in the values of the entropy difference for FeO between two boundary pressures from the beginning of the stability of the B8 phase of the oxide until the end of the Earth's lower mantle with a change in temperature

However, starting from the Earth's lower mantle, the opposite of all of this happens. For the pressure value of 23.8342 GPa, the entropy values begin to decrease immediately. As for the pressure of 65.5202 GPa, the value of entropy does not decrease until after a temperature of 1881 K, where its value reaches a limit value estimated at joule/K.mole 69.71.

The entropy values for the first value of pressure are the highest up to a temperature estimated at 1762 K, where its value reaches the value of convergence between them, which is estimated at joule/K.mole 69.693. This decrease continues until the end of the Earth's lower mantle, with an increasing difference starting from the last mentioned temperature, before which the difference decreases. The minimum entropy change width for this oxide is for the pressure 65.5202 GPa, with the following estimate joule/K.mole 0.48.

The entropy values at the boundaries between the layers are approximately equal, if the difference is very small. The value of this difference between the boundaries of the Mohorovici region is estimated at 0.48 joule/K.mole, and it is more than a hundred times smaller than that at the boundaries between the two parts of the Earth's mantle.

IV- Conclusion:

After studying the change in the Debye temperature of iron oxide and its effect on its phase transformation, we were able to see the change in some of the parameters involved in the thermodynamic properties, which are internal and free energies, heat capacity with constant volume, and entropy. We concluded the following:

- A clear effect of the Debye temperature on the phase transformation of these oxides, whose values are always increasing in its first phase and are higher than those in its second phase. Where the pressure increases until the pressure is 120 GPa, after which the values of this temperature decrease. Using the linear change approximation between every two successive pressure values, the Debye temperature values of the oxide were determined at the pressures of the PREM model representative of the ground material. Therefore, the change of the studied parameters was calculated from the thermodynamic properties at the boundary pressures of the layers that included the study boundaries.

The changes in the internal and free energies of the oxide usually agree, as they do not differ except in the direction of the change and the magnitude of the values and their sign, of course.

Through this study, we were not able to determine what happens to the change in parameters between the two pressures, 70 to 80 GPa, and the same problem occurred in the study approved for us.

It is unfortunate that the results of our calculations were not compared with other calculations or the results of experimental calculations, due to their unavailability.

In the future, the results of this study can be used to calculate other parameters, such as heat capacity at constant pressure, thermal expansion, thermal conductivity, etc.

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